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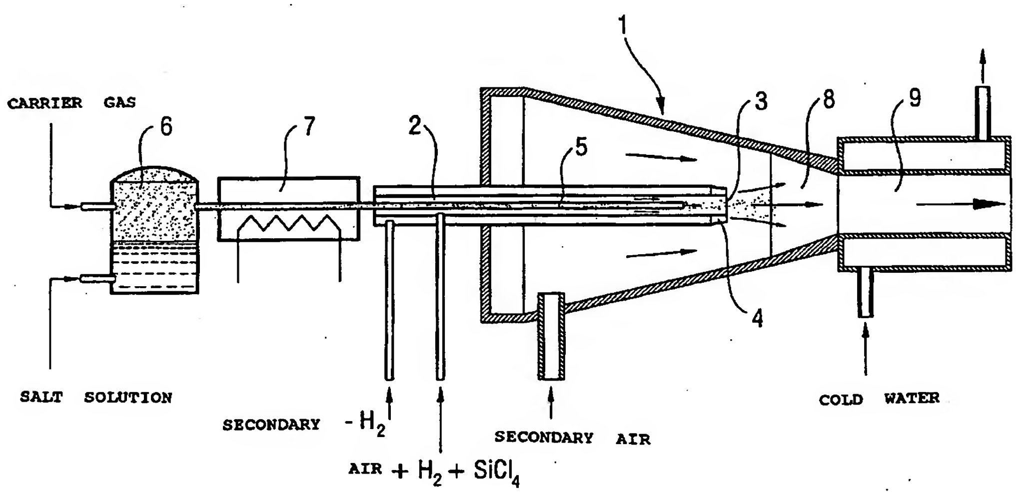
(54) **DIOXYDE DE SILICIUM PRODUIT PAR PYROGENATION ET DOPE A L'AIDE D'UN AEROSOL**

(54) **PYROGENICALLY PRODUCED SILICON DIOXIDE DOPED BY MEANS OF AN AEROSOL**



(57) Pyrogenically produced silicon dioxide doped with aluminium oxide by means of an aerosol is produced by including an aqueous aerosol of an aluminium salt in the reaction during flame hydrolysis. The silicon dioxide doped with Al_2O_3 by means of an aerosol may inter alia be used in the production of inkjet paper.

Abstract

Pyrogenically produced silicon dioxide doped with aluminium oxide by means of an aerosol is produced by including an aqueous aerosol of an aluminium salt in the reaction during flame hydrolysis.

The silicon dioxide doped with Al_2O_3 by means of an aerosol may *inter alia* be used in the production of inkjet paper.

Figure 2

Pyrogenically produced silicon dioxide doped by means of an aerosol

This invention relates to pyrogenically produced silicon dioxide doped with aluminium oxide by means of an aerosol, which silicon dioxide is very readily dispersible in polar media, and to a process for the production thereof, and to the use thereof in papermaking, in particular in inkjet paper and inkjet film. The invention furthermore relates to the use thereof for the production of low viscosity dispersions or for the production of highly-filled dispersions.

Extremely readily dispersible fillers, which for example in inkjet paper or inkjet film absorb the ink well and retain the brilliance of the colours, are required for use in the paper industry.

It is known to dope pyrogenically produced silica in the flame in one step in a specific process (DE 196 50 500 A1, EP-A 0 850 876). This process comprises a combination of high temperature flame hydrolysis with pyrolysis. This doping process should be distinguished from the prior, so-called "co-fumed process", in which the gaseous starting products (for example $SiCl_4$ gas and $AlCl_3$ gas) are premixed and jointly combusted in a flame reactor, wherein pyrogenically produced mixed oxides are obtained.

The products produced using the two different processes exhibit distinctly differentiated applicational properties.

In the doping process used according to the invention, an aerosol is introduced into a flame, in which an oxide is being produced by flame hydrolysis, wherein this aerosol contains a salt of the compound to be doped.

It has now been found that when aluminium compounds dissolved in water are used as the starting product for the aerosol to be introduced, a pyrogenically produced silica doped with aluminium oxide is obtained as the product, which is extremely readily dispersible in polar media, such as water and is highly suitable for use in inkjet paper and film.

The present invention provides a pyrogenically produced silica doped with aluminium oxide by means of an aerosol, which silica is characterised in that the basic component is a silica produced pyrogenically using a flame oxidation method or preferably flame hydrolysis method, which component is doped with a doping component of 1×10^{-4} and up to 20 wt.%, wherein the doping quantity is preferably in the range from 1 to 10000 ppm and the doping component is a salt or mixture of salts of aluminium or a suspension of an aluminium compound or metallic aluminium or mixtures thereof, wherein the BET surface area of the doped oxide is between 5 and 600 m^2/g, preferably in the range between 40 and 100 m^2/g.

The silica according to the invention may have a DBP value of below 100 g/100 g.

The present invention also provides a process for the production of the pyrogenically produced silicas doped with aluminium oxide by means of an aerosol, which process is characterised in that an aerosol is introduced into a flame, as is used for the pyrogenic production of silica by the flame oxidation method or preferably flame hydrolysis method, the aerosol is homogeneously mixed with the flame oxidation or flame hydrolysis gas mixture before the reaction, then the aerosol/gas mixture is allowed to react in the flame and the resultant pyrogenically produced silicas doped with aluminium oxide are separated from the gas stream in a known manner, wherein the aerosol is

produced using an aqueous solution which contains salts or mixtures of salts of aluminium or the metal itself in dissolved or suspended form or mixtures thereof, wherein the aerosol is produced by atomisation by means of a two-fluid nozzle or by another aerosol production method, preferably by an aerosol generator using ultrasound atomisation.

Salts which may be used are: $AlCl_3$, $Al_2(SO_4)_3$, $Al(NO_3)_3$.

The flame hydrolysis processes for the production of pyrogenic oxides and thus also for the production of silicon dioxide (silica) are known from Ullmanns Enzyklopädie der technischen Chemie, 4th edition, volume 21, page 464.

The present invention also provides the use of the pyrogenically produced silica doped by means of an aerosol as a filler, in particular in the paper industry for the production of inkjet paper and inkjet film or other inkjet materials, such as for example canvas, plastic films etc., as a support material, as a catalytically active substance, as a starting material for the production of dispersions, as a polishing agent (CMP applications), as a ceramic base material, in the electronics industry, as a filler for polymers, as a starting material for the production of glass or glass coatings or glass fibres, as a release auxiliary even at elevated temperatures, in the cosmetics industry, as an absorbent, as an additive in the silicone and rubber industry, for adjusting the rheological properties of liquid systems, for heat stabilisation, as a thermal insulating material, as a flow auxiliary, as a filler in the dental industry, as an auxiliary in the pharmaceuticals industry, in the lacquer industry, in PET film applications, in fluorescent tubes, as a starting material for the production of filter ceramics or filters.

The present invention also provides blends of 0.1 to 100% of the silicas according to the invention with other pyrogenically produced or precipitated silicas or bentonites or other fillers or mixtures of these fillers conventional in the paper industry.

The silica according to the invention, which is, for example, obtained as the product when aluminium chloride salts dissolved in water are used to produce the aerosol to be introduced, may very readily be dispersed in polar media, such as for example water. The silica is accordingly suitable for use in the production of inkjet paper and inkjet films. It is possible using the doped, pyrogenically produced silicon dioxide dispersed in water to apply transparent or glossy coatings onto inkjet media, such as paper or film.

The silicon dioxide according to the invention and the process for the production thereof as well as the use thereof are illustrated and described in greater detail by means of Figure 1 and the following Examples:

Figure 1 is a schematic representation of the doping apparatus. The central component of the apparatus is a burner of a known design for the production of pyrogenic oxides.

The burner 1 consists of the central tube 2, which opens into the nozzle 3, from which the main gas stream flows into the combustion chamber and combusts therein. The nozzle 3 is surrounded by the annular nozzle 4, from which the (annular or secondary) hydrogen flows.

The axial tube 5 is located in the central tube 2, which axial tube finishes a few centimetres before the nozzle of the central tube 2. The aerosol is introduced into the axial tube 5.

The aerosol, which consists of an aqueous aluminium chloride solution, is produced in an aerosol generator 6 (ultrasound atomiser).

The aluminium chloride/water aerosol produced in the aerosol generator 6 is passed by means of a gentle carrier gas stream through the heating zone 7, in which the entrained water vaporises, wherein small salt crystals remain in the gas phase in finely divided form.

Example 1

Production of a pyrogenically produced silica doped with aluminium oxide by means of an aerosol and having a low BET surface area.

5.25 kg/h of $SiCl_4$ are vaporised at approx. 130 °C and transferred into the central tube 2 of the burner 1. 3.47 Nm^3/h of (primary) hydrogen and 3.76 Nm^3/h of air are additionally introduced into the central tube 2. 0.95 Nm^3/h of oxygen are additionally added to this mixture.

The gas mixture flows from the nozzle 3 of the burner 1 and burns in the combustion chamber and the water-cooled flame tube connected thereto.

0.5 Nm^3/h of (jacket or secondary) hydrogen as well as 0.3 Nm^3/h of nitrogen are introduced into the annular nozzle 4.

20 Nm^3/h of (secondary) air are also additionally introduced into the combustion chamber.

The second gas stream flows from the axial tube 5 into the central tube 2.

The second gas stream consists of the aerosol, which is produced by ultrasound atomisation of $AlCl_3$ solution in the aerosol generator 6. The aerosol generator 6 here atomises

460 g/h of 2.29% aqueous aluminium trichloride solution. The aluminium chloride aerosol is passed through the heated line with the assistance of 0.5 Nm^3/h of air as carrier gas, wherein the aqueous aerosol is converted into a gas and salt crystal aerosol at temperatures of approx. 180 °C.

At the mouth of the burner, the temperature of the gas mixture ($SiCl_4$/air/hydrogen, water aerosol) is 156 °C.

The reaction gases and the pyrogenic silica doped with aluminium oxide by means of an aerosol are drawn through the cooling system by application of reduced pressure. The particle/gas stream is consequently cooled to approx. 100 to 160 °C. The solids are separated from the exit gas stream in a cyclone.

The pyrogenically produced silica doped with aluminium oxide by means of an aerosol is obtained as a white, finely divided powder.

In a further step, any still adhering residues of hydrochloric acid are removed from the silica at elevated temperature by treatment with air containing steam.

The BET surface area of the pyrogenic silica doped with aluminium oxide is 55 m^2/g.

Table 1 summarises the production conditions. Table 2 states further analytical data for the silica according to the invention.

Example 2

Production of a pyrogenically produced silica doped with aluminium oxide by means of an aerosol and having an elevated BET surface area.

4.44 kg/h of $SiCl_4$ are vaporised at approx. 130 °C and transferred into the central tube 2 of the burner 1 of a

known design. 3.15 Nm^3/h of (primary) hydrogen and 8.2 Nm^3/h of air are additionally introduced into the central tube 2.

The gas mixture flows from the nozzle 3 of the burner 1 and burns in the combustion chamber and the water-cooled flame tube connected thereto.

0.5 Nm^3/h of (jacket or secondary) hydrogen and 0.3 Nm^3/h of nitrogen are introduced into the annular nozzle 4.

12 Nm^3/h of (secondary) air are also additionally introduced into the combustion chamber.

The second gas stream flows from the axial tube 5 into the central tube 2.

The second gas stream consists of the aerosol, which is produced by ultrasound atomisation of $AlCl_3$ solution in the separate atomising unit 6. The aerosol generator 6 here atomises 450 g/h of 2.29% aqueous aluminium trichloride solution. The aluminium chloride aerosol is passed through the heated line with the assistance of 0.5 Nm^3/h of air as carrier gas, wherein the aqueous aerosol is converted into a gas and salt crystal aerosol at temperatures of approx. 180 °C.

At the mouth of the burner, the temperature of the gas mixture ($SiCl_4$/air/hydrogen, water aerosol) is 180 °C.

The reaction gases and the pyrogenically produced silica doped with aluminium oxide by means of an aerosol are drawn through a cooling system by application of reduced pressure. The particle/gas stream is consequently cooled to approx. 100 to 160 °C. The solids are separated from the exit gas stream in a cyclone.

The pyrogenically produced silica doped with aluminium oxide by means of an aerosol is obtained as a white, finely

divided powder. In a further step, any still adhering residues of hydrochloric acid are removed from the silica at elevated temperature by treatment with air containing steam.

The BET surface area of the pyrogenic silica doped with aluminium oxide by means of an aerosol is 203 m^2/g.

Table 1 shows the production conditions. Table 2 states further analytical data for the silica according to the invention.

Table 1

Experimental conditions during the production of pyrogenic silica doped with aluminium oxide

No.	$SiCl_4$ kg/h	Primary air Nm^3/h	O_2 centre Nm^3/h	Sec.. air Nm^3/h	H_2 centre Nm^3/h	H_2 jacket Nm^3/h	N_2 jacket Nm^3/h	Gas temp. °C	Salt solution	Aerosol quantity kg/h	Air aeros. Nm^3/h	BET m^2/g
1	5.25	3.76	0.95	20	3.47	0.5	0.3	156	2.29% aqueous $AlCl_3$	0.46	0.5	55
2	4.44	8.2	0	12	3.15	0.5	0.3	180	2.29% aqueous $AlCl_3$	0.45	0.5	203

Legend: Primary air = quantity of air in central tube; Sec. air = secondary air; H_2 centre = hydrogen in central tube; Gas temp. = gas temperature at the nozzle of the central tube; Aerosol quantity = mass flow rate of the salt solution converted into aerosol form; Air aeros. = carrier gas (air) quantity of the aerosol;

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Table 2

Analytical data of the specimens obtained according to Examples 1 to 2

	BET m^2/g	pH value 4% susp.	Tamped density g/l	DBP absorption g/100 g	Al_2O_3 content wt.%	SiO_2 content wt.%	Chloride content ppm		
Example no. 1	55	4.39	94	81	0.187	99.79	89		
Example no. 2	203	4.15	24	326	0.27	99.67			
By way of comparison									
Aerosil OX 50	50	3.8 to 4.8	130	approx. 160	<0.08	>99.8	<250		

Legend: pH 4% susp. = pH value of the 4% aqueous suspension

Electron micrograph:

Figure 2 shows an electron micrograph of the pyrogenic silica doped with aluminium oxide by means of an aerosol according to Example 1.

It is striking that there are numerous individual spherical primary particles, which have not intergrown.

The difference between the pyrogenic silicas doped with aluminium oxide by means of an aerosol according to the invention and pyrogenic silicas produced using a known method and having the same specific surface area is in particular revealed by the DBP absorption, which is a measure of the "structure" of the pyrogenic silica (i.e. of the degree of intergrowth).

The commercially available silica OX 50 produced using the pyrogenic high temperature flame hydrolysis process thus exhibits DBP absorption of approx. 160 (g/100 g) (at a BET surface area of 50 m^2/g), while the pyrogenic silica doped with 0.187 wt.% of Al_2O_3 according to the invention exhibits DBP absorption of only 81 (g/100 g). The very low DBP absorption means that low viscosity dispersions may be produced from the pyrogenic silica doped with aluminium oxide according to the invention. By virtue of these properties, dispersions having an elevated filler content may straightforwardly be produced.

Moreover, particular note should be taken of the excellent dispersibility and incorporability of the silica according to the invention.

This is advantageous, especially for use as an absorbent filler in papermaking, which should also be taken to include use in inkjet paper and inkjet film.

Transparent and glossy coatings may also be produced from the dispersions of the silicas according to the invention.

Table 3 shows the difference in incorporation behaviour and viscosity.

The following, commercially available pyrogenic oxides and mixed oxides are used by way of comparison (all products of Degussa, Frankfurt): Aerosil 200 (pyrogenically produced silica), MOX 170 (pyrogenically produced aluminium/silicon mixed oxide), Aluminiumoxid C (pyrogenically produced aluminium oxide).

Table 3

Name	Aerosil A 200	MOX 170	Alu C	Example 1	Example 2
SiO_2 content [wt.%]	>99.8	>98.3	<0.1	99.79	99.67
Al_2O_3 [wt.%]	<0.05	0.8	>99.6	0.187	0.27
BET [m^2/g]	200	170	100	55	203
DBP absorption [g/100 g]	330	332	230	81	325
Incorporability [--]	moderate to difficult	mode-rate	mode-rate	very good	moderate
Viscosity [mPas] at 5 rpm at 100 rpm	4560 1200	880 420	560 330	400 210	14480 2570
BET before sintering and after 3 hours' sintering at 1150°C [m^2/g]	200 17	170 43		55 50	203 125
Bulk density before sintering and after 3 hours' sintering at 1150°C [g/l]	40 160	40 220		73 80	17 26

Incorporability refers to the speed with which the powder may be stirred into a given liquid.

In comparison with the known pyrogenically produced mixed oxide MOX 170, which contains >98.3 wt.% of silicon dioxide and 0.8 wt.% of Al_2O_3 and is produced by flame hydrolysis of a mixture of $AlCl_3$ and $SiCl_4$, the pyrogenically produced silicon dioxide doped by means of an aerosol according to the invention exhibits distinctly reduced sintering activity.

As is evident from Table 3, the known pyrogenically produced oxides, such as Aerosil 200 (silicon dioxide) and MOX 170 (Al_2O_3/SiO_2 mixed oxide), sinter together with a distinct increase in bulk density, wherein the BET surface simultaneously falls sharply.

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In contrast, the pyrogenically produced silicon dioxides doped by means of an aerosol according to the invention exhibit only a slight change in bulk density after sintering. This means that the silicon dioxides according to the invention have a distinctly reduced sintering activity.

Viscosity was determined in a 15%, relative to solids content, aqueous dispersion. The solids content is here composed of the following parts:

50 parts by weight of the pyrogenic silica as well as 30 parts by weight of Mowiol 28-99 (polyvinyl alcohol, Cassella-Höchst) and 50 parts by weight of Lumiten PPR 8450 (polyvinylpyrrolidone, BASF).

The 15% aqueous suspension is stirred for 30 minutes at 3000 rpm in a high-speed stirrer, then allowed to stand for 24 hours, then briefly stirred by hand and measured at 23 °C using a Brookfield viscosimeter (model RVT), with spindle size being adapted to the particular viscosity.

Evaluation of printing behaviour:

A commercially available film (Kimoto 105 g/m^2) is coated with this 15% dispersion after 10 days (with brief shaking) using a no. 4 coating knife and is printed with a Hewlett-Packard 550 C printer. Print quality is assessed visually. (Best mark = 1, worst mark = 6)

Tables 4 and 5 show the results for three-colour printing and four-colour printing.

Table 4: Three-colour printing (All Colour) HP 550 C

Name	**Aerosil A 200**	**MOX 170**	**Alu C**	**Example 1**	**Example 2**
Colour intensity M/G/C black	1 1	1 1	1 1	1 1	1 1.75
Dot sharpness Black in colour	1.5	1.75	1.75	1.75	1.5
Transitions Colour in colour	1	1	1	1	1
Dot sharpness Black print	1	1	1	1	1.75
Dot sharpness Black outlines	1.5	1.5	1	1	1.5
Continuous tone printing Colour intensity/ Outlines	1	1	1.75	1.5	1
Total evaluation	8	8.25	8.5	8.25	8.5
Average evaluation	**1.14**	**1.17**	**1.21**	**1.17**	**1.21**

M/G/C: Magenta, green, cyan

Table 5: Four-colour printing (Black and Colour) HP 550 C

Name	**Aerosil A 200**	**MOX 170**	**Alu C**	**Example 1**	**Example 2**
Colour intensity M/G/C black	1 1	1 1	1 1	1 1	1 1
Dot sharpness Black in colour	3.5	3.5	1.5	3	3.5
Transitions Colour in colour	1	1	1	1	1
Dot sharpness Black print	1	1	1	1	1
Dot sharpness Black outlines	1.5	1.75	1.75	2	1.75
Continuous tone printing Colour intensity/ Outlines	1.5	1.5	1.5	1.5	1.5
Total evaluation	10.5	10.75	9.5	10.5	9.75
Average evaluation	**1.5**	**1.5**	**1.4**	**1.5**	**1.4**

In principle, blends of the silicas according to the invention with other pyrogenically produced or precipitated silicas or bentonites or other fillers or mixtures of these fillers conventional in the paper industry are also possible.

Patent Claims:

1. Pyrogenically produced silica doped with aluminium oxide by means of an aerosol,
c h a r a c t e r i s e d i n t h a t ,
the basic component is a silica produced pyrogenically using a flame oxidation method or flame hydrolysis method, which component has been doped with a doping component of 1×10^{-4} and up to 20 wt.%, wherein the doping quantity is preferably in the range from 1 to 10000 ppm and the doping component is a salt or mixture of salts of aluminium or a suspension of an aluminium compound or metallic aluminium or mixtures thereof, wherein the BET surface area of the doped oxide is between 5 and 600 m^2/g.

2. Process for the production of the pyrogenically produced silica doped with aluminium oxide by means of an aerosol according to claim 1,
c h a r a c t e r i s e d i n t h a t
an aerosol is introduced into a flame, as is used for the pyrogenic production of silica by the flame oxidation method or flame hydrolysis method, the aerosol is homogeneously mixed with the flame oxidation or flame hydrolysis gas mixture before the reaction, then the aerosol/gas mixture is allowed to react in the flame and the resultant pyrogenically produced silicas doped with aluminium oxide are separated from the gas stream in a known manner, wherein the aerosol is produced using an aqueous solution which contains salts or mixtures of salts of aluminium or the metal itself in dissolved or suspended form or mixtures thereof, wherein the aerosol is produced by atomisation by means of a two-fluid nozzle or by another aerosol production method.

3. Use of the pyrogenically produced silica doped with aluminium oxide by means of an aerosol as a filler, in particular in the paper industry for the production of inkjet paper and inkjet film or other inkjet materials, as a support material, as a catalytically active substance, as a starting material for the production of dispersions, as a polishing agent (CMP applications), as a ceramic base material, in the electronics industry, as a filler for polymers, as a starting material for the production of glass or glass coatings or glass fibres or melting crucibles, as a release auxiliary even at elevated temperatures, in the cosmetics industry, as an absorbent, as an additive in the silicone and rubber industry, for adjusting the rheological properties of liquid systems, for heat stabilisation, as a thermal insulating material, as a flow auxiliary, as a filler in the dental industry, as an auxiliary in the pharmaceuticals industry, in the lacquer industry, in PET film applications, in fluorescent tubes, as a starting material for the production of filter ceramics or filters, in toner powders, as an antirust agent, as an agent for film coating polyethylene (PE) and polyvinyl acetate (PVA), in inks, in battery separators.

4. Blends of 0.01 to 100% of the silicas according to claim 1 with other pyrogenically produced or precipitated silicas or bentonites or other fillers or mixtures of these fillers conventional in the paper industry.

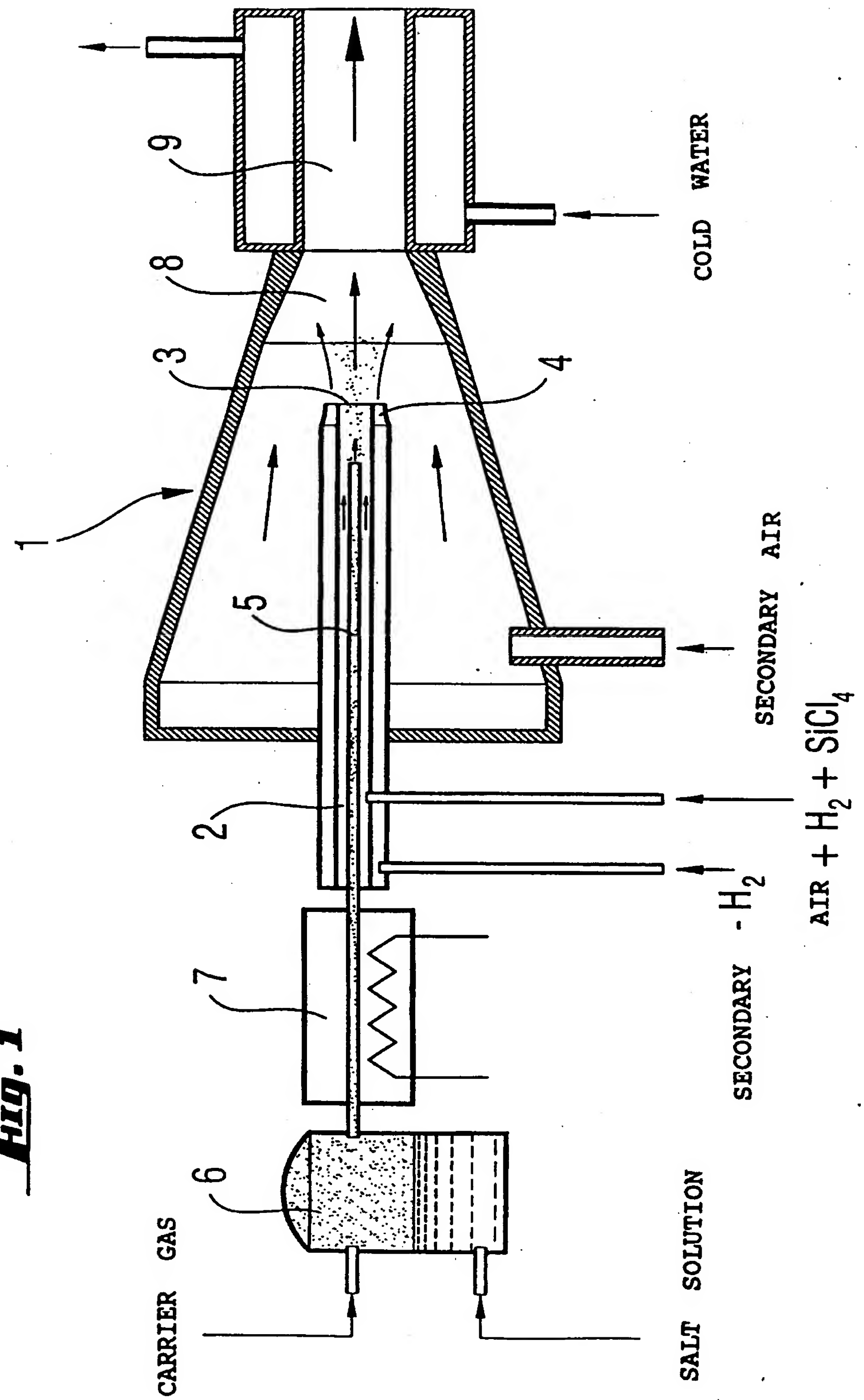

Fig. 1

Marks & Clerk

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Fig. 2

Marks eO